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A theory of free induction decay in polymer melts: Beyond the limits of the second cumulant approximation

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Abstract

The correlation function F(t) describing the free induction decay in melts of polymers with the molecular mass exceeding the critical molecular mass of entanglement formation is calculated within the framework of the quantum mechanical perturbation theory. Neglect of multispin correlations is shown to yield a significantly overestimated value for the F(t) decay rate. The transverse relaxation rate in polymer melts is numerically estimated on the basis of the reptation model and the twice renormalized Rouse model. The ratio between the theoretical and experimental transverse relaxation times is found to vary from 0.53 to 5.30. A comparison with the experiment showed that the reptation model yields an upper estimate for the intensity of the entanglement forces in melts of high-molecular-mass polymers, and the twice renormalized Rouse model yields a lower estimate for it.